

Granular activated carbons from broiler manure: physical, chemical and adsorptive properties [☆]

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Abstract

Broiler manure produced at large concentrated facilities poses risks to the quality of water and public health. This study utilizes broiler litter and cake as source materials for granular activated carbon production and optimizes conditions for their production. Pelletized manure samples were pyrolyzed at 700 °C for 1 h followed by activation in an inert atmosphere under steam at different water flow rates, for a period ranging from 15 to 75 min. Carbon physical and adsorptive properties were dependent on activation time and quantity of steam used as activant, yields varied from 18% to 28%, surface area varied from 253 to 548 m²/g and copper ion adsorption varied from 0.13 to 1.92 mmol Cu²⁺/g carbon. Best overall performing carbons were steam activated for 45 min at 3 ml/min. Comparative studies with commercial carbons revealed the broiler cake-based carbon as having the highest copper ion efficiency.

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Keywords: Activated carbon; Broiler manure; Copper ion remediation

1. Introduction

Growing awareness and concern from the impact of animal wastes on the quality of life and the environment is capturing the attention of researchers towards developing alternative methods of waste reduction and reuse. In the United States, a predicted 8.6 billion broilers will be produced in 2004 (NASS, 2004) generating approximately 9 million metric tons of manure. Broiler management involves their confinement in concentrated animal facilities which usually results in excessive localized land application of this manure due to over production. This

situation may pose a threat to public health and the environment because of potential contamination of air, ground and surface water sources via run-off and odor releases. Other manure uses, beside land application, such as burning for fuel recovery or land filling, produce low-value alternatives. Out of 3.7 million miles of streams and rivers in the US, farming impairs water quality to some degree in 18% of the 0.7 million miles that states and tribes assessed during 2000 (EPA Water Quality Assessments Report to Congress, 2000). When specifying the type of agricultural activity, animal feeding operations were reported to degrade up to 25,000 river and stream miles (EPA Water Quality Assessments Report to Congress, 2000).

A potentially profitable alternative method for animal waste re-use is the manufacture of activated carbons. This value-added approach transforms the hazard prone waste into a high porosity, high surface area material used in industry for purification and

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chemical recovery operations, as well as environmental remediation. Activated carbons can be produced from a number of precursor materials including coal, peat, wood and agricultural wastes. Coal and coconut shells are the most common precursors and they are expensive, non-renewable or not readily available in the US. The production of granular activated carbons, GAC's, from animal waste can serve two important purposes: utilize large amounts of animal manure produced in concentrated areas and convert it into useful value-added adsorbents. There is a growing interest in removing metals from wastewater, groundwater, and drinking water. Commercial carbons, while excellent at adsorbing various organic constituents from air or water, have limited ability to remove metals. Various nutshells have been studied as sources for good metal adsorbing carbons, such as almond, pecan, macadamia, and walnut. Almond and pecan shell-based carbons that are good metal ion adsorbents (Johns et al., 1999; Toles et al., 1998, 2000a,b,c) have been developed by a patented process involving concurrent phosphoric acid activation and air oxidation at temperatures between 400 and 500 °C (Toles et al., 2000c). The effectiveness of these carbons was shown to be highly dependent upon activation conditions whether it is steam, carbon dioxide or acid activation, followed by oxidation (Johns et al., 1999). The activation of these nutshell-based carbons using steam or CO₂ does not particularly enhance metals adsorption without added oxidation (Johns et al., 1998).

Studies have been conducted for over 20 years to analyze the feasibility of less traditional wastes, as sources of activated carbons, such as municipal sludges and animal manures. Bilitewski (1979) analyzed activated carbons made from both industrial and agricultural wastes; municipal biosolids, waste tires, paper mill waste and poultry droppings, for percent ash, percent volatiles, pH and surface area among others after degasification at 700 °C. The poultry droppings carbon had a surface area of 60.5 m²/g of carbon and carbon content of 27.5%. The overall assessment was that these precursors produce a very low grade carbon due mainly to the high ash content (Bilitewski, 1979). Subsequent studies have looked at organics adsorption from various types of chemically activated municipal sludges (Chiang and You, 1987; Jeyaseelan and Qing, 1996; Tay et al., 2001a,b and Chen et al., 2002). These authors looked at the use of zinc chloride, ZnCl₂ to improve the carbon's specific surface area and adsorption capacity. Chiang and You (1987) found that adding 5 M ZnCl₂ to treated sludge and heating the mixture to 550 °C for 1 h achieved the optimum conditions with regard to specific surface area and adsorption capacity for organic vapors. Jeyaseelan and Qing (1996) obtained the highest surface area (309 m²/g) with 5 M ZnCl₂. Carbons from sludge were found to have approximately 25% the capacity of commercial grade carbons (Jeyaseelan and

Qing, 1996). Tay et al. in 2001 examined the effect of mixing coconut husks with anaerobically digested sewage sludge. Again, the highest surface area was produced with a 5 M ZnCl₂ activation and pyrolysis at 500 °C for 2 h under nitrogen atmosphere and with a heating rate of 10 °C/min. Under these conditions, the resulting carbon exhibited a surface area of 868 m²/g and a phenol removal efficiency of 58%. The optimum cost-effective materials ratio was found to be 1:4 (Tay et al., 2001a). Martin et al. (1996) used ZnCl₂ and H₂SO₄ as chemical activants and compared their effectiveness by measuring specific surface area, yield, pore size distribution and, phenol adsorption capabilities of carbons made from secondary sludge from a domestic wastewater treatment plant. The best results (surface area of 257 m²/g) were obtained with H₂SO₄ in a 1:1 w/w ratio, but, five times more activated carbon from sludge was required to achieve the same phenol removal as the commercial grade carbons. Chen et al. (2002) obtained a phenol adsorption approximately 25% that of commercial grade carbons with a 5 M ZnCl₂ activation of anaerobically digested sludge, but the capacity for CCl₄ was at a similar level with commercial carbons. Overall, these studies report adsorption capacities/efficiencies for organic species, by municipal sludge carbons that still lag behind their commercial counterparts. There are no reports in the literature of GACs made from any type of animal manure, with enhanced adsorption for metals. Therefore, the conversion of broiler manure to activated carbon could represent a novel approach to animal waste utilization.

Our objectives in this study were: (1) to convert broiler litter and broiler cake to activated carbon for possible use as a metal ion adsorbent; (2) evaluate the resulting carbons for their physical, chemical and copper ion adsorptive properties as affected by activation conditions; and (3) to compare the sample carbons with two different commercially available carbons in order to determine the relative efficacy of the broiler manure carbon in relation to its commercial counterparts.

2. Methods

2.1. Precursor materials

Broiler litter and broiler cake samples were obtained from the USDA-ARS, Poultry Research Unit (Starkville, MS). Samples and their respective carbons were sent to an outside Laboratory (Central Analytical Laboratories, Belle Chase, LA) for elemental analysis (carbon, nitrogen, phosphorous, potassium, sulfur, ash and moisture). Broiler litter and broiler cake are the same manure, and differentiation is made based on the presence of small amounts of wood shavings in litter (5–30%) and none to very small amounts in cake

(<5%). Wood shavings are utilized as bedding material. Samples were either re-hydrated or dried if moisture fell outside of a 20–35%, determined to be ideal for efficient pelletization of this type material. Samples were ground in a Retsch cross-beater mill (Glen Mills, Clifton, NJ) to less than 1 mm particle size and pelletized in a PMCL5 Lab pellet mill (California Pellet Mill, CPM, Merrimack, NH) with a 3/16 in die plate. Pellet moisture content was analyzed using a Sartorius Moisture Analyzer MA 51 (Brentwood, NY).

Two commercial carbons with enhanced metal ion adsorption ability were studied for comparison purposes: Minotaur was obtained from Calgon Carbon Corporation in Pittsburgh, PA and PUR RF (replacement filter) was obtained from a local retail outlet. Minotaur is made from bituminous coal and PUR RF comes in block form and is also coal derived. Both samples were sieved to 18 × 40 mesh size.

2.2. Activation method

Pelletized poultry litter samples were pyrolyzed and activated using a Lindberg bench furnace (Lindberg/Blue M, with retort, Waterton, WI). Pellets were pyrolyzed at 700 °C under nitrogen gas (flow rate of 0.1 m³/h) for 1 h prior to steam activation. Steam activation involved injecting water at various flow rates (1, 3 or 5 ml/min), using a peristaltic pump, into a nitrogen gas flow entering the heated retort. Chars (pyrolyzed pellets) were activated at 800 °C for 15, 30, 45, 60 or 75 min. Both water flow rates and activation times were varied to achieve different activation conditions. Samples were allowed to cool to room temperature overnight and the carbon yield was recorded. Samples were washed with 0.1 N HCl to remove surface ash, water rinsed three times and dried overnight at 80 °C.

2.3. Physical measurements: BET surface area, bulk density and attrition

Broiler litter and cake-based carbons were ground to 18 × 40 mesh size, using a mortar and pestle. With the exception of surface area measurements (done on pellets) and kinetic studies (done on 80 × 170 mesh samples), all measurements were done on 18 × 40 mesh samples, which are still considered granular rather than powdered carbons. The BET (Brunauer–Emmett–Teller) surface area measurements were obtained from nitrogen adsorption isotherms at 77 K using a Nova 2000 Quantachrome Surface Area Analyzer (Boynton Beach, FL). Specific surface areas (S_{BET}) were taken from adsorption isotherms using the BET equation. The micropore size distributions were calculated using t -plots derived from the Nova 2000 software.

Apparent (bulk) density of all samples was determined by filling a 10-ml tube with sample, 1 ml at a time,

capping and tapping to a constant (minimum) volume. The apparent density (g/cm³) was calculated as the ratio between weight and volume of packed dry material.

To determine attrition (decrease in particle size due to usage), 1 g of sample was placed in 100 ml of deionized water, stirred at 500 rpm for 24 h and screened through a 60-mesh screen. Percent attrition was measured as the ratio between the material not retained by the screen and the initial sample weight.

2.4. Metals adsorption

All adsorption results reported are the average of two replicates. Copper ion adsorption was of particular interest because copper is one of the metals of environmental concern. It is toxic to many animal species and is an environmentally ubiquitous metal found in both drinking water and wastewater. Equilibrium binding assays were carried out with 0.25 g of GACs (18–40 mesh) stirred with Teflon coated, magnetic stir-bars at 300 rpm in 25 ml of a cupric chloride (CuCl₂·2H₂O) 20 mM solution for 24 h. The solution was made up in 0.07 molar sodium acetate–0.03 molar acetic acid buffer (pH 4.8). The pH of the slurry was recorded at the beginning and at the end of the experiment and the final pH of the carbon slurries was 4.8 ± 0.5. An aliquot of the solution was drawn off in a disposable syringe, and filtered through a 0.22 µm Millipore filter to remove any suspended material. The sample was diluted to 1:100 by volume with 4 vol% HNO₃ (Trace metal grade) and analyzed by inductively coupled plasma (ICP) spectroscopy using a Leeman Labs Profile sequential ICP (Leeman Labs, Hudson, NH). Aliquots were taken at specific time intervals (5 min, 1, 4 and 24 h) for kinetic studies.

2.5. Total titrable negative surface charge

Surface charge measurements for all samples were taken at pH 5.0. One gram of GAC was suspended in 100 ml of deionized water. Sample pH was adjusted to 5.0 by adding 0.1 N NaOH. After reaching the desired pH, samples were rinsed on a #50 sieve for 2 min and transferred to a petri dish to be dried overnight at 80 °C. A titrimetric method based on Boehm (1994) was modified to identify total titrable negative surface charge for the carbons. The method involved suspending 0.25 g of carbon in 25 ml of 0.1000 ± 0.0005 N NaOH and stirring in a closed vessel for 24 h. After this time, the slurry was filtered and a 10 ml aliquot was added to 15 ml of 0.1000 ± 0.0005 N HCl. The HCl neutralized the unreacted NaOH and kept further reaction between atmospheric carbon dioxide and NaOH from occurring. The solution was then back-titrated with 0.1000 ± 0.0005 N NaOH using Bromothymol Blue as an indicator. The volume of NaOH required to neutralize the sample was converted to titrable negative surface charge

with results expressed as mmol H⁺ equivalent/g carbon, from the following equation

$$C_s = U_b R_b N / M_c \quad (1)$$

where C_s = surface charge per weight of adsorbent in mmol H⁺ eq/g, U_b = difference in NaOH uptake between titrated sample and titrated blank, R_b = ratio of base volume in original slurry to filtrate volume used in titration, N = normality of HCl and M_c = weight of carbon in grams.

3. Results and discussion

3.1. Development of broiler litter and broiler cake-based carbons

The present study utilized broiler litter and broiler cake for the manufacture of activated carbons that were evaluated for copper ion adsorption. Optimum pyrolysis and activation conditions for the preparation of broiler litter and broiler cake-based carbons were investigated. Optimum conditions were selected based on a combination of high adsorption, high surface area and high yield. The physical data on the carbons manufactured from pelletized broiler litter and boiler cake as a function of activation conditions are summarized in Table 1. Elemental analysis for both broiler litter and broiler cake carbons is shown in Table 2.

Both the activation time and flow rate were varied to produce a range of carbons of varying characteristics. For each set of activation conditions, carbon yield was higher for litter-based carbons (29.1% for 3 ml/min, 45 min activation) than cake-based carbons (25.0% for 3 ml/min, 45 min activation) (Table 1). The higher carbon yield for litter-based carbons can be explained by the presence of small amounts of wood shavings in broiler litter, which increase the amount of carbon in the starting material from 17.2% (cake-based carbon) to 25.8% (litter-based carbon) (Table 2). Because wood is a dense material, during pyrolysis and activation, the litter pellet is volatilized to a lesser extent and undergoes less weight loss than the cake pellet. Yield was directly influenced by activation conditions, decreasing with length of activation as well as water flow rate (Table 1) ranging between 25.2% and 34.7% for litter-based carbons and 24.6% and 34.9% for cake-based carbons for 60 min at 5 ml/min and 30 min at 1 ml/min, respectively.

3.2. Carbon physical properties: attrition, bulk density and surface area

Physical properties for the experimental carbons are displayed in Table 1. All experimental carbons displayed high attrition values (Table 1) because of the nature of the precursor material utilized. Animal manure is a rel-

atively soft material. On average, attrition was slightly higher for cake-based carbons (83.9–97.1%) than litter-based carbons (76.2–93.6%) due to a higher amount of carbon in the former. Experimental carbons also displayed higher attrition than their commercial counterparts. Carbon friability can lead to carbon loss during its use, make regeneration potentially difficult, and slow down filtration rates in column applications. However, attrition can be reduced significantly by incorporating an appropriate high quality binder into the pelletization process. Agricultural wastes such as sugarcane or sugar beet molasses are inexpensive and renewable choices for a binder.

Bulk density for the experimental carbons did not vary significantly with activation conditions (Table 1). However, bulk density declined with the progression of activation due to porosity development. Surface areas ranged between 364 and 493 m²/g and 253 and 548 m²/g for cake-based carbons and litter-based carbons, respectively (Table 1). Surface area development occurred rapidly, with activation times as low as 15 min, producing surface areas close to the highest values observed. Beyond 15 min, activation did not result in further significant increase in surface area. For the highest water flow rate in the study (5 ml/min), the surface area decreased with further activation. Samples were significantly washed for the most severe treatment conditions with obvious negligible development of surface area (Table 1). Because poultry manure is not a dense material, the activation process is facilitated and occurs much faster than with other more common carbon precursors, such as coal or coconut shells. This outcome is desirable because short activation times result in reduced manufacturing costs. Conversely, being a soft material limits the development of very large surface areas. Surface areas for the experimental carbons were lower than for the commercial carbons.

3.3. Carbon adsorption properties

The evolution of copper ion adsorption with activation conditions is depicted in Fig. 1. Significant copper ion removal occurred at the shortest activation time under study (15 min). This was particularly true for broiler cake-based carbons, where for a 5 ml/min activation, 1.56 mmol Cu²⁺ were adsorbed per g of GAC from a solution containing 2.0 mmol Cu²⁺ (Table 3). As activation progressed, and samples were further activated to a total of 45 min, copper adsorption was nearly complete with 1.92 mmol Cu²⁺ adsorbed per g in the same solution containing 2.0 mmol Cu²⁺ for broiler-cake-based carbons (Table 3). Beyond 45 min of activation, no further improvements in copper ion adsorption were observed for both broiler cake- and litter-based carbons. Because of almost complete removal of copper ion from solution for samples activated for 45 min, activating be-

Table 1

Physical properties of broiler cake and litter carbons produced by variation in activation time and water flow rate, and some commercial adsorbents

Sample	FR (ml/min)	AT (min)	Y (%)	Ash (%)	SA (m ² /g)	MA (m ² /g)	PM (%)	BD (g/cm ³)	A (%)
Cake	1	15	37.9	28.0	364	320	88	0.53	89.8 ± 1.1
		30	34.9	31.8	440	377	86	0.51	97.1 ± 1.3
		45	34.1	30.9	415	361	87	0.51	93.1 ± 0.6
		60	31.2	35.5	478	397	83	0.54	87.0 ± 0.6
	3	15	35.8	39.7	457	408	89	0.50	88.9 ± 12.5
		30	31.9	37.7	446	385	86	0.54	83.9 ± 16.3
		45	28.7	59.0	481	357	74	0.52	96.5 ± 0.8
		60	26.0	75.7	419	289	69	0.55	90.8 ± 3.1
	5	15	33.8	36.3	486	422	87	0.47	91.6 ± 8.0
		30	29.1	53.6	493	348	71	0.50	95.5 ± 1.7
		45	25.7	79.2	377	250	66	0.57	96.9 ± 0.5
		60	24.6	88.3	—	—	—	—	—
Litter	1	30	34.7	24.7	374	329	88	0.53	87.2 ± 3.7
		45	32.4	30.4	446	386	87	0.47	89.5 ± 2.7
		60	31.5	27.2	432	373	86	0.36	88.7 ± 2.9
		75	29.5	28.7	422	349	83	0.41	92.0 ± 2.4
	3	30	33.0	26.0	419	366	87	0.57	80.9 ± 10.8
		45	30.8	28.0	445	344	77	0.55	90.2 ± 1.2
		60	28.6	52.1	548	359	66	0.44	93.6 ± 0.5
		75	25.5	67.6	450	277	61	0.46	89.1 ± 0.3
	5	30	31.3	27.5	443	380	86	0.52	82.4 ± 17.3
		45	27.5	32.8	377	252	67	0.50	88.8 ± 9.3
		60	25.2	58.3	317	150	47	0.54	92.2 ± 1.1
		75	22.6	82.5	253	107	42	—	83.4 ± 1.7
Minotaur					844	717	85	0.49	78.9 ± 11.4
PUR RF			—		511	444	87	0.42	55.4 ± 15.3

FR = water flow rate, AT = Activation time, Y = carbon yield, SA = BET surface area, MA = micropore area, PM = percentage of micropores, BD = bulk density, A = attrition.

Table 2

Elemental analysis of broiler litter and cake and their respective carbons, on a percent basis

	Total carbon (%)	Nitrogen (%)	Sulfur (%)	Potassium (%)	Phosphorous (%)	Ash (%)	Moisture content (%)
Broiler litter, BL	34.4	3.26	0.67	3.8	1.7	20.3	3.5
Broiler cake, BC	32.6	3.62	0.83	5.3	1.9	20.6	5.7
BL carbon	25.8	0.75	0.64	3.0	4.8	64.9	0.88
BC carbon	17.2	0.60	0.80	5.8	7.3	74.4	0.82

yond 45–60 min was unnecessary. Moreover, further activation was detrimental because it led to reduced yield with no additional increase in the surface area of the carbon. Because significantly reduced yield values were observed for activations beyond 60 min for cake-based carbons, adsorption studies were not pursued for these samples. For litter-based carbons, decreased adsorption was observed beyond 45 min activation for the 3 and 5 ml/min flow rate samples (Fig. 1). Adsorption was also flow rate dependent, with increased copper ion uptake with increased flow rate (Fig. 1). This could result from a faster development of surface area with increased water flow rates. A large surface area is an important requirement particularly for the adsorption

of non-polar organic molecules, but surface area alone does not explain the high uptake in copper ion by the experimental carbons. This was evident by the lack of correlation between copper ion adsorption and surface area. It is believed that the high adsorption values exhibited by the experimental carbons are related to charge–charge interactions that lead to metal ion sequestration (Lima and Marshall, 2004). This is caused by the presence of surface functional groups, which for the case of copper ion adsorption, would be negatively charged. Because samples containing large amounts of titratable surface functional groups usually display high surface charge, this study looked at total negative surface charge (in mmol H⁺ eq/g carbon) at pH values of 3, 5, and 7

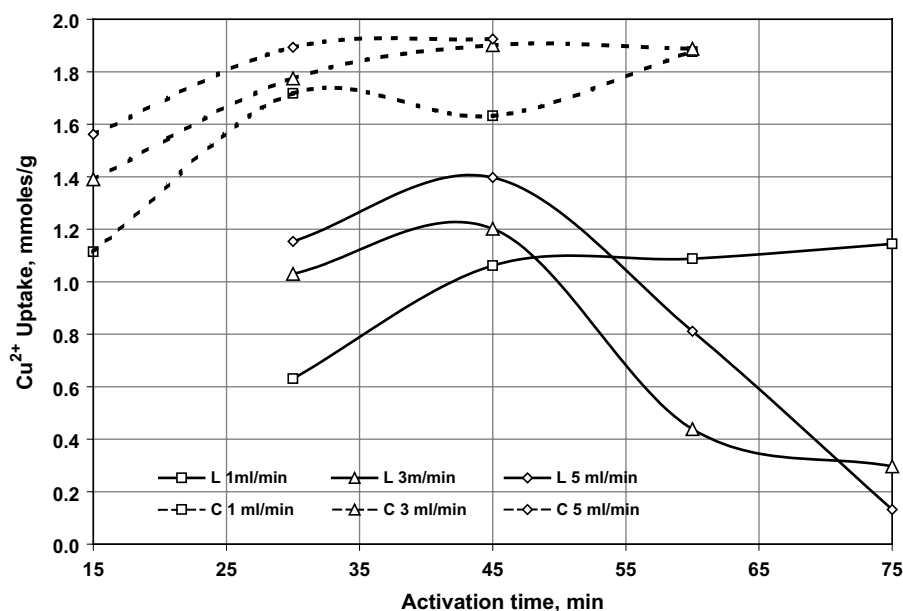


Fig. 1. Copper adsorption as a function of activation conditions for broiler cake (C)- and broiler litter (L)-based carbons. 1, 3, and 5 are the water flow rates in ml/min during activation.

Table 3

Adsorption efficiencies for broiler cake- and litter-based carbons and for two commercial samples in mmol/g carbon \pm SD

	AT (min)	FR (ml/min)		
		1	3	5
Cake	15	1.11 \pm 0.11	1.39 \pm 0.17	1.56 \pm 0.02
	30	1.72 \pm 0.05	1.77 \pm 0.15	1.89 \pm 0.02
	45	1.63 \pm 0.08	1.90 \pm 0.02	1.92 \pm 0.02
	60	1.88 \pm 0.01	1.89 \pm 0.03	
Litter	30	0.63 \pm 0.02	1.03 \pm 0.21	1.15 \pm 0.02
	45	1.06 \pm 0.05	1.20 \pm 0.04	1.40 \pm 0.03
	60	1.09 \pm 0.02	0.44 \pm 0.04	0.81 \pm 0.10
	75	1.14 \pm 0.06	0.30 \pm 0.05	0.13 \pm 0.05
Minotaur		0.93 \pm 0.01		
PUR RF		0.28 \pm 0.00		

AT: activation time; FR: flow rate.

(Table 4). Total negative surface charge for the experimental carbons was much lower than would be expected from the adsorption results. Minotaur's relatively high adsorption for Cu^{2+} , can be explained by its total negative surface charge, but the same cannot be said for the experimental carbons. Both broiler litter- and broiler cake-based carbons displayed adsorption values consistently higher and for some samples significantly higher than Minotaur. However, they failed to exhibit strong negative surface charge. More studies need to be pursued to establish why broiler litter and broiler cake-based carbons have such a high affinity for the positively charged copper ion. Elemental analysis data done on broiler litter, broiler cake and their respective carbons reveals that elemental phosphorous was the only inor-

ganic species that was present in higher amounts in the carbon (Table 2). Broiler cake carbon also contained much more phosphorous than broiler litter. It is hypothesized that phosphorous does play an important, if not fundamental role in the adsorption process. In chemical activated carbons, it has been proposed that phosphoric acid appears to combine with organic species to form phosphate and polyphosphate bridges that connect and crosslink biopolymer fragments (Jagtoyen and Derbyshire, 1998). Phosphorous is probably present in the functional chemical groups responsible for the sequestration of positively charged copper ion. At this point more data are needed to identify these groups.

Experimental carbons were further characterized by looking at their kinetics. For instance, when carbons

Table 4

Carbon surface charge at pH 3, 5 and 7 for broiler litter and broiler cake-based carbons and for two commercial samples, in mmol H⁺ eq/g carbon

	FR	AT	pH		
			3	5	7
Cake	1	30	0.48	0.86	0.82
		45	0.90	0.68	0.80
	3	30	0.69	0.65	0.69
		45	0.94	1.04	0.95
	5	30	0.86	0.53	0.94
		45	0.75	0.70	0.74
Litter	1	30	0.00	0.27	0.47
		45	0.72	0.47	0.37
	3	30	0.32	0.47	0.20
		45	0.17	0.32	0.05
	5	30	0.49	0.96	0.95
		45	0.77	0.84	0.29
Minotaur			2.87	2.62	1.88
PUR-RF			0.55	0.10	0.00

AT: activation time; FR: flow rate.

are used in flow systems for industrial wastewater treatment, studies of time taken to adsorb in static systems are of interest. In those cases it is important for the carbon to adsorb as much of the metal ion as possible as well as rapidly as possible. Broiler cake-based carbon (45 min activation at 5 ml/min) rated best for the shortest contact time in the study, being the only sample that adsorbed in excess of 0.50 mmol of Cu²⁺ ion during the first 5 min of exposure. Fast adsorption kinetics are

desirable when it may not be possible to extend the contact time between the activated carbon and the adsorbate, such as in a fast flowing column or contactor. In the kinetic analysis of the carbons, a two-phase reaction was evident when plotting equilibrium adsorbate concentration versus time (Fig. 2). From Fig. 2, it was possible to identify these two distinct regions, each one displaying significantly different adsorption rates. A zero order reaction was apparent for each phase, where adsorption occurred independent of concentration. From this plot, adsorption rates for each phase (K_1 and K_2) were determined and are reported in Table 5 in mmol L⁻¹ h⁻¹.

Each adsorption site has associated adsorption energy. Adsorption will initially occur preferentially at the sites that have the maximum adsorption potential, that is, sites with the highest energy of adsorption. As adsorption progresses in time, these high energy sites are occupied and the adsorbate will continually adsorb onto the next higher energy sites available. The process continues until the lowest energy of adsorption sites are utilized. The amount, distribution and availability of adsorption sites of varying adsorption potential varies significantly with the carbon source. For the broiler-based carbons, the first region occurred for the first 30 min of adsorption and the second one occurred for adsorption times beyond 30 min. For the commercial carbons, the first phase lasted approximately 1 h. The K_1 rate constant was extremely high for the broiler-based carbon (39.6 mmol L⁻¹ h⁻¹), meaning that this carbon was at least three times faster at adsorbing copper ion than Minotaur, and more than 10 fold faster than PUR RF. For the second stage, the superiority of the broiler-based carbon was also observed with a K_2

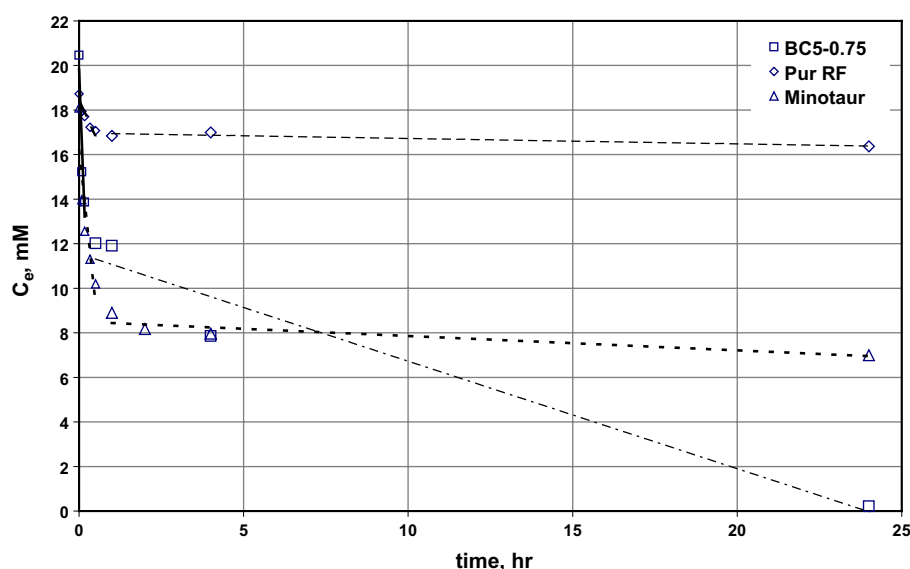


Fig. 2. Kinetic decay in equilibrium copper ion concentration with time for a broiler cake-based carbon (BC5-0.75) and two commercial carbons (Pur RF and Minotaur). BC5-0.75 represents broiler cake-based carbon activated for 45 min at 5 ml/min.

Table 5

Kinetic rate constants in $\text{mmol L}^{-1} \text{h}^{-1}$, designated K_1 and K_2 , (zero order reaction) and corresponding regression coefficients (R^2) for broiler cake-based carbon and two commercial carbons

	K_1	R^2	K_2	R^2
Broiler cake, BC	39.6	0.90	0.50	0.95
Minotaur	13.7	0.80	0.07	0.82
PUR RF	3.0	0.86	0.02	0.87

rate constant of $0.5 \text{ mmol L}^{-1} \text{h}^{-1}$, when compared to 0.07 and $0.02 \text{ mmol L}^{-1} \text{h}^{-1}$ for Minotaur and PUR RF, that is, a 7- and a 25-fold difference, respectively (Table 5). The results of Table 5 re-confirm the superiority of the broiler manure-based carbons when compared to their commercial counterparts.

4. Conclusions

This study produced GACs from pelletized broiler litter and cake using steam activation, and looked at the effects of water flow rate and activation time on selected physical, chemical and adsorptive properties of the carbons. The conversion of broiler manure to activated carbons and their use for metal ion remediation represents a novel approach to the utilization of broiler manure. Results indicate that pelletized broiler litter or cake can be pyrolyzed and steam activated to produce granular activated carbons with excellent adsorption capacity for copper ion. The set of activation conditions resulting in the best performing carbon in terms of yield, surface area and copper ion adsorption was a 45 min activation at a water flow rate of 3 ml/min. All experimental carbons displayed high attrition values due to absence of a binder. GACs made from broiler cake proved to be more effective in adsorption of copper ion from water than either commercial carbon (Minotaur and PUR RF) included in this study. These carbons displayed the highest adsorption efficiencies for copper ion (up to $1.92 \text{ mmol Cu}^{2+}/\text{g}$ carbon), outperforming the two commercial carbons. These results demonstrate the potential of broiler manure GAC as an inexpensive wastewater filter for copper ion.

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